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PAPER

In situ study of electrochemical activation and surface segregation of the SOFC electrode material $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3\pm\delta}$†

Anne-Katrin Huber,[a] Mareike Falk,[a] Marcus Rohnke,[a] Bjoern Luerßen,[a] Luca Gregoratti,[b] Matteo Amati[b] and Jürgen Janek*[a]

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Mixed-conducting perovskite-type electrodes which are used as cathodes in solid oxide fuel cells (SOFCs) exhibit pronounced performance improvement after cathodic polarization. The current *in situ* study addresses the mechanism of this activation process which is still unknown. We chose the new perovskite-type material $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3\pm\delta}$ which is a potential candidate for use in symmetrical solid oxide fuel cells (SFCs). We prepared $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3\pm\delta}$ thin film model electrodes on YSZ (111) single crystals by pulsed laser deposition (PLD). Impedance spectroscopy (EIS) measurements show that the kinetics of these electrodes can be drastically improved by applying a cathodic potential. To understand the origin of the enhanced electrocatalytic activity the surfaces of operating LSCrM electrodes were studied *in situ* (at low pressure) with spatially resolving X-ray photoelectron spectroscopy (μ-ESCA, SPEM) and quasi static secondary ion mass spectrometry (ToF-SIMS) after applying different electrical potentials in the SIMS chamber. We observed that the electrode surfaces which were annealed at 600 °C are enriched significantly in strontium. Subsequent cathodic polarization decreases the strontium surface concentration while anodic polarization increases the strontium accumulation at the electrode surface. We propose a mechanism based on the reversible incorporation of a passivating SrO surface phase into the LSCrM lattice to explain the observed activation/deactivation process.

Introduction

Solid Oxide Fuel Cells (SOFCs) have the great advantage—in contrast to other fuel cell systems—of operating with a wide variety of different fuels like petroleum, diesel and natural gas. This can only be achieved by sufficiently stable electrolyte and electrode materials. State-of-the-art SOFC components are $La_{0.8}Sr_{0.2}MnO_3$ (LSM) and other perovskite-type cathodes due to their excellent electronic conductivity and good electrocatalytic activity for the oxygen reduction reaction (ORR), Y_2O_3-stabilized ZrO_2 (YSZ) as electrolyte and the Ni/YSZ cermet anode, which offers excellent electrocatalytic properties for fuel oxidation.

Typically, the cathode and anode are separated by the electrolyte and the cathode is only exposed to the oxidizing atmosphere. Under operation the cell reaction drives an oxygen ion flux towards the anode, molecular oxygen is consumed and reduced at the cathode, and depending on the cathode kinetics the local oxygen activity at the three phase boundary may be lower than fixed by the oxygen partial pressure in the gas phase (deviation from local equilibrium), thus leading to reducing conditions.[1] The widely used cathode material $La_{1-x}Sr_xMn_yO_{3\pm\delta}$ is not stable under reducing conditions, and thus under operation degradation may occur and can lead to reduced efficiency, or even complete failure of cathodes. A new type of cathode material which can operate stable under both oxidizing and reducing atmospheres could be a solution to this problem and would simplify the cell construction. In essence, a new symmetrical design of SOFCs could be achieved, with the same electrode material used for the preparation of both the cathode and anode.

Recently Irvine[2,3] demonstrated promising results with chromium doped lanthanum strontium manganate perovskites (LSCrM) as effective anode and cathode material for symmetrical SOFCs (SFCs). Commonly, lanthanum chromates ($LaCrO_3$) are used as interconnectors in SOFCs because of their stability and good electronic conductivity under oxidizing and reducing conditions at high temperatures. Replacement of lanthanum with alkaline earth metals like strontium or calcium creates oxygen vacancies and increases the electronic

[a] *Institute of Physical Chemistry, Justus-Liebig University, 35392, Gießen, Germany. E-mail: Juergen.Janek@phys.Chemie.uni-giessen.de; Fax: +49 6419934509; Tel: +49 9934501*
[b] *Sinchrotrone Elettra, 34012, Basovizza-Trieste, Italy. E-mail: luca.gregorattix@elettra.trieste.it; Fax: +39 0403758565; Tel: +39 0403758025*
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conductivity due to charge compensation of Cr^{3+} to Cr^{4+} so that their properties are tailored for the application as cathode and anode in SOFCs.

In comparison with the standard anode material (Ni/YSZ cermet anode) which reveals low sulfur tolerance and catalyzes the formation of carbon in natural hydrocarbons, LSCrM anodes exhibit a low tendency towards carbon deposition and sulfur poisoning.[4,5]

Accepting LSCrM electrodes as a reasonable and promising new electrode material, current research efforts aim to improve the electrocatalytic activity and the cell efficiency. Much less is known about long term stability and degradation effects based on surface segregation and diffusion processes.

Therefore, we focused in the present work on the electrochemical performance of LSCrM electrodes under cathodic polarization, studied by impedance spectroscopy, quasi *in situ* ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and *in situ* SPEM (Scanning X-ray Photoelectron Microscopy). Activation effects upon cathodic polarization have been often reported for LSM electrodes but up to now the origin of this effect is still under debate. In the following we present results which indicate that the electrochemical activation in LSCrM is accompanied by severe surface composition changes.

In order to perform well reproducible experiments and to allow spectroscopic access to the TPB (three phase boundary) and neighboring electrode regions, we prepared geometrically well defined model electrodes by pulsed laser deposition (PLD). SPEM and ToF-SIMS were used to monitor the effect of electrochemical polarization on the surface composition of the electrode. It is important to note that all spectroscopic measurements have been performed at reduced pressure, thus, for comparison with observations at atmospheric pressure one has to take the ''pressure gap'' into account.

Experimental section

Sample preparation

Square thin film electrodes with an area of 1 cm^2 were deposited onto (111) orientated YSZ single crystalline substrates (*CrysTec, Germany*) by pulsed laser deposition. The $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ powder was prepared by a citrate sol–gel route (see ESI†).

Electrochemical setup

Polarization measurements were performed in a two-electrode arrangement (Fig. 1) with a porous Pt counter electrode (CE) symmetrically arranged opposite to the working electrode (WE) to minimize errors in electrochemical measurements.[7,8] Impedance measurements were performed at open circuit in the frequency range from 0.1 Hz to 10 kHz with a signal amplitude of 10 mV with a VersaStat.^{3}400 potentiostat (*Princeton Applied Research*). The electrode area was 1 × 1 cm^2.

The polarization experiments were started by applying a constant cathodic potential of −2.5 V for different periods at 800 °C at ambient pressure in a tube furnace. The electrode resistance R was determined directly by the difference of the high and low frequency intercept with the real axis from the impedance data.

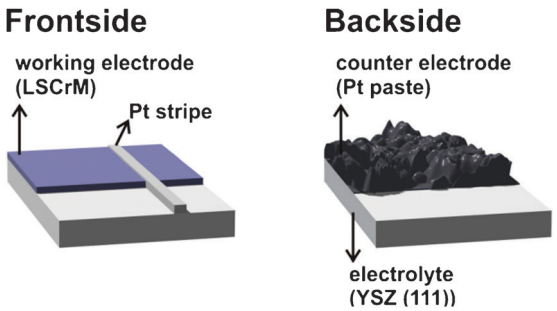

Fig. 1 Schematic diagram of the cell configuration for the two electrode measurements used in this study.

In situ XPS

High resolution X-ray photoelectron spectroscopy and scanning microscopy (XPS/SPEM) were performed at the ESCA microscopy beamline at the ELETTRA synchrotron light facility in Trieste, Italy.[9,10] For the polarization experiments the samples were heated in the ESCA chamber up to 600 °C with an oxygen partial pressure of 10^{-6} mbar. The XPS and SPEM measurements were carried out with the Sr 3d, Mn 3p, Cr 3p and La 4d signals after Ar^+ bombardment to remove surface contaminations. The binding energy scale was adjusted by the position of the Fermi level to compensate possible changes due to the electrochemical polarization. After Shirley type background correction the spectra were fitted by using XPSPeak4.0 software. The experimental setup is depicted in Fig. 2. Full experimental details are given in the ESI.†

Quasi *in situ* SIMS

For SIMS measurements a ToF.SIMS^5 machine (IonTOF, Münster, Germany) was used. A detailed implementation of the used SIMS technique is given in the ESI.† The LSCrM samples were heated up to 500 °C in the SIMS chamber with an oxygen partial pressure of 10^{-6} mbar. The polarisation potentials were applied by a Keithley 2004 SourceMeter and

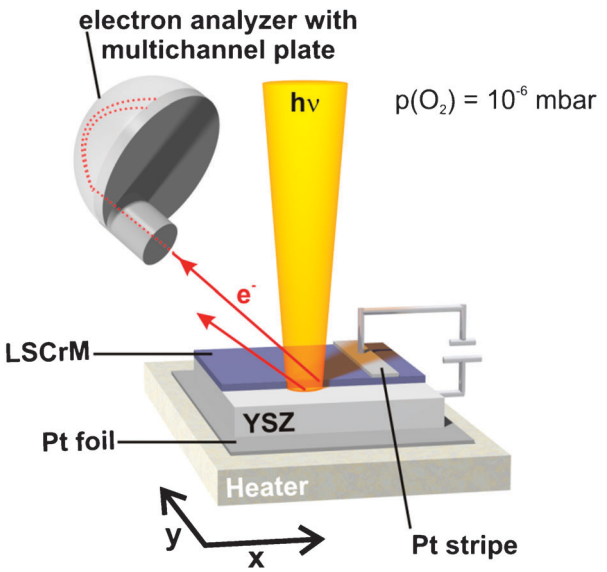

Fig. 2 Experimental setup for the *in situ* XPS measurements at Elettra synchrotron light facility in Trieste.

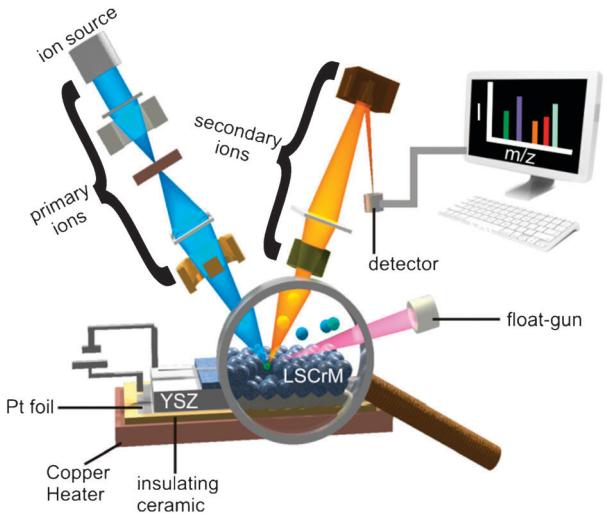

Fig. 3 Experimental setup for the ToF-SIMS measurements.

after continuous polarization for 30 minutes the samples were quickly cooled down to minimise the background in the SIMS spectra, and the measurements were performed. Successive heating/polarisation/cooling cycles were performed in order to check the reproducibility of the experiments. All spectra and images were standardized and analyzed with the ToF-SIMS software V4.1 (Fig. 3).

Results

Impedance measurements

Fig. 4 shows the impedance spectra of a freshly prepared $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ electrode on YSZ (111) before (black dots) and after electrochemical activation by cathodic polarization with a constant electrochemical potential of −2.5 V for different times.

Before any electrochemical polarisation the impedance response is characterized by three overlapping semi circles.

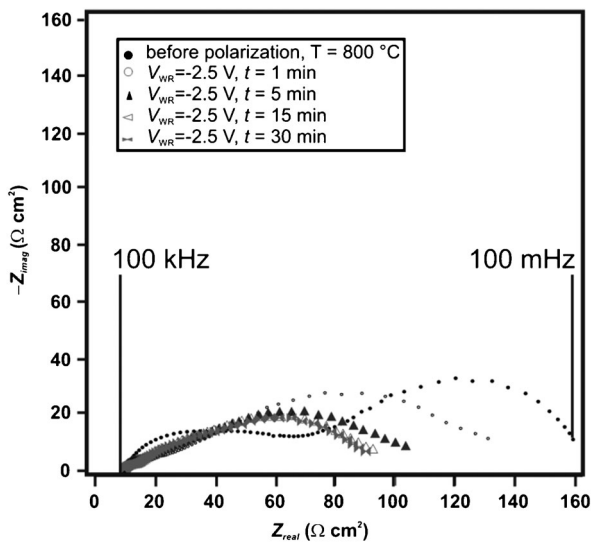

Fig. 4 Impedance for the oxygen reduction reaction (ORR) at a LSCrM electrode (1 × 1 cm^2) after cathodic polarization with V_{WC} = −2.5 V as a function of time at ambient pressure.

According to the literature[11] the O_2 reduction reaction can be considered to occur in three elementary steps, and each circle can be assigned as follows:

1. The low-frequency intercept characterizes the electrochemical oxygen surface exchange reaction consisting of dissociative adsorption of oxygen at the electrode surface, ionization of adsorbed oxygen to O^{2-} ions and incorporation of oxide ions into the mixed conducting electrode material.

2. The mid-frequency part can be assigned to oxygen ion transfer processes, mainly diffusion of adsorbed oxygen ions to the three phase boundary. Additionally, the formation of reaction products between LSCrM and YSZ like $La_2Zr_2O_7$ and $SrZrO_3$ might influence this part of the spectrum, but due to the low preparation and operation temperature used in this study, the formation of these phases is excluded.

3. The high-frequency circle contains information on the charge transfer process and the incorporation of oxide ions into oxygen vacancies of the electrolyte. The shift of the spectrum on the real axis corresponds to the electrolyte resistance.

Several authors[12–15] have shown that various parameters influence the impedance response of perovskite electrodes on YSZ. The absolute values of the different resistances and capacities depend strongly on preparation conditions, thermal treatment and the electrochemical history that cannot be controlled exactly and be kept constant during the experimental procedure. But as we focus on the correlation between electrochemical behavior and surface/interface composition rather than on the optimization of electrode properties, the absolute data required to describe the electrode impedance are not relevant.

The polarization resistance of freshly prepared LSCrM electrodes was found to be about 150 Ohm cm^2. Upon application of a cathodic potential of −2.5 V the impedance decreases mainly in the first few minutes of polarization. After one minute of cathodic activation the polarization resistance was reduced to 120 Ohm cm^2, being 20% smaller than the initial one (Fig. 4). With advancing time the activation effect became smaller, and after cathodic polarization for 15 minutes the polarization resistance remained constant.

Studies on LSM/YSZ electrodes[6,16] showed that the oxygen surface exchange reaction is strongly affected by surface segregation processes of strontium and manganese. To identify the origin of activation of our model electrodes, we performed *in situ* XPS and SIMS measurements at $p(O_2) = 10^{-6}$ mbar.

XPS measurements

The surface composition of LSCrM thin film electrodes under different applied potentials was examined by XPS to get a closer look into the mechanism of electrochemical activation. The effect of electrochemical polarization on the surface concentration of the different elements was analyzed by determination of the different relative peak areas of Sr 3d, Cr 3p, Mn 3p, La 4d and Zr 4d. As the sensitivity factors for the different elements in the system LSCrM are not exactly known, only relative changes were analyzed.

Fig. 5 depicts high resolution XPS spectra of the Sr 3d peak as a function of different applied voltages monitored on the LSCrM (left) and YSZ (right) surface with a distance of 50 μm away from the interface.

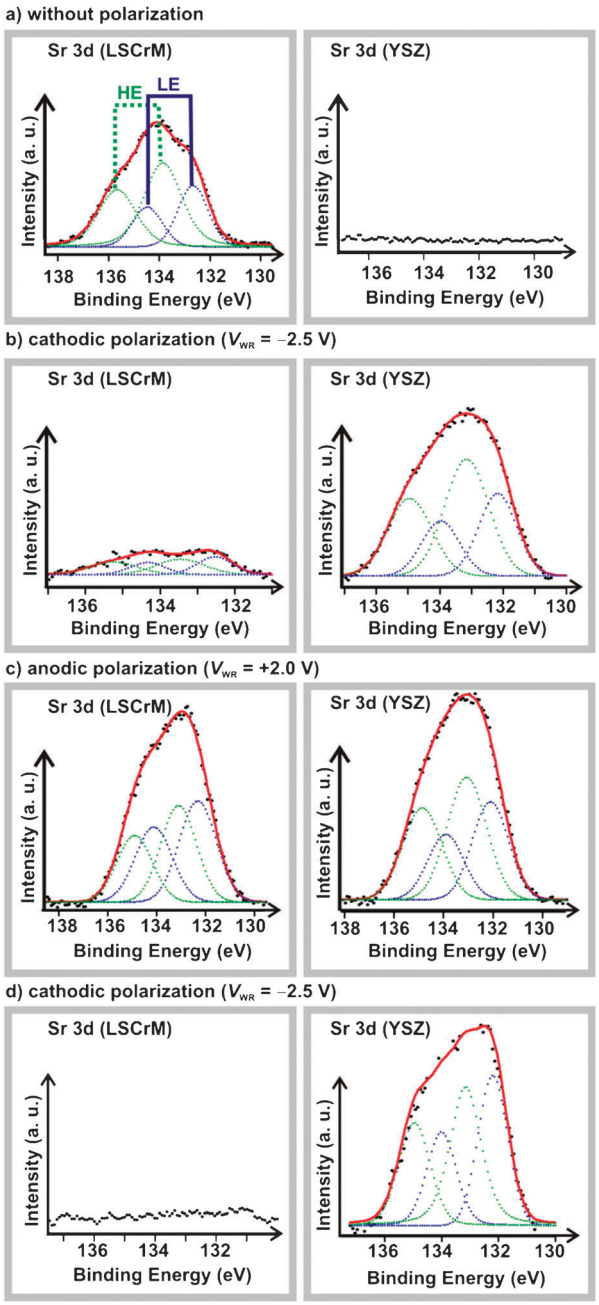

Fig. 5 Sr 3d spectra monitored *in situ* on the LSCrM (left) and the YSZ (right) surface with a distance of 50 μm away from the interface (tpb) at 600 °C under different applied voltages (HE = high binding energy component, LE = low binding energy component).

Under cathodic polarization depletion of the LSCrM surface in strontium occurs. Subsequent anodic polarization leads to a reversible segregation process and the surface becomes rich in strontium in comparison to the freshly prepared sample. A second cathodic polarization causes the complete depletion in strontium so that no Sr 3d peak can be identified. It is important to note that under cathodic polarization the surface strontium peak disappeared on the LSCrM surface while a pronounced Sr 3d peak appears on the YSZ surface. During the following experiments the Sr 3d peak on the YSZ remained constant. Therefore, we conclude that the surface diffusion and

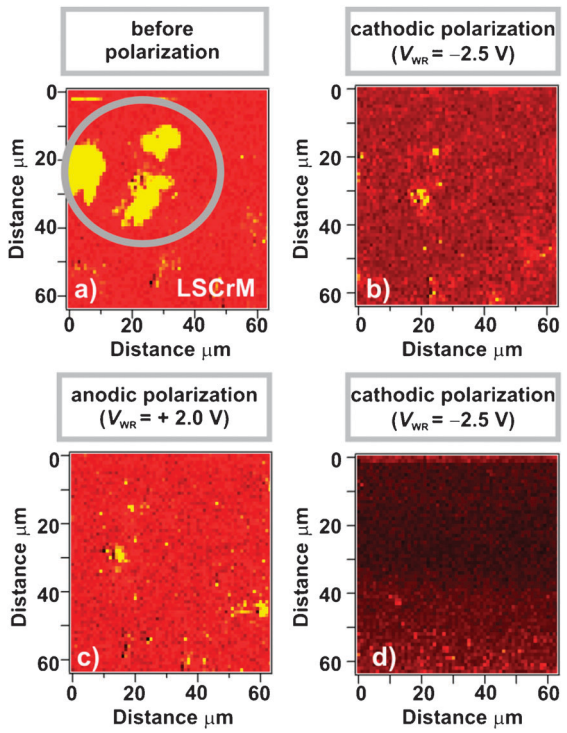

Fig. 6 SPEM images of the Sr 3d component monitored on the LSCrM surface for different applied voltages. In the images bright colours denote high strontium concentration and dark colours characterize areas with a low strontium level.

spreading of strontium under cathodic polarization from the LSCrM onto the YSZ is an irreversible process.

Two components separated by 1.2 eV are required to fit the Sr 3d spectrum. The origin for the additional high binding energy component (HE) or the so-called "surface core level shift (SCS)" is the existence of a surface species of strontium. The emission of this surface state differs from that for strontium in the bulk of the electrode.[18]

Cathodic polarization influences the component at high binding stronger than the low binding so that mainly surface related strontium will be removed by cathodic bias.

Additionally, Fig. 6 presents SPEM images of the LSCrM surface as prepared (a) and with different applied bias (b–d). The electrochemically untreated state already shows small surface areas with enhanced strontium concentration (strontium islands). During electrochemical polarization the strontium islands disappear under cathodic polarization and a re-segregation of Sr onto the LSCrM surface occurs with applied anodic bias.

In analogy to the XPS observations in the case of strontium, we also found that the surface concentration of manganese depends on the applied potential. Under cathodic polarization a surface depletion of manganese occurs, and a reversible diffusion process takes place under anodic bias (Fig. 7). Diffusion of manganese from the LSCrM surface onto the YSZ cannot be verified unequivocally as only a small Mn 3p peak appears in the spectra which cannot be separated accurately from the background.

The Mn 3p peak appears as an unresolved doublet and is accompanied by a satellite peak on the high binding energy side. According to the literature[19] these satellite features

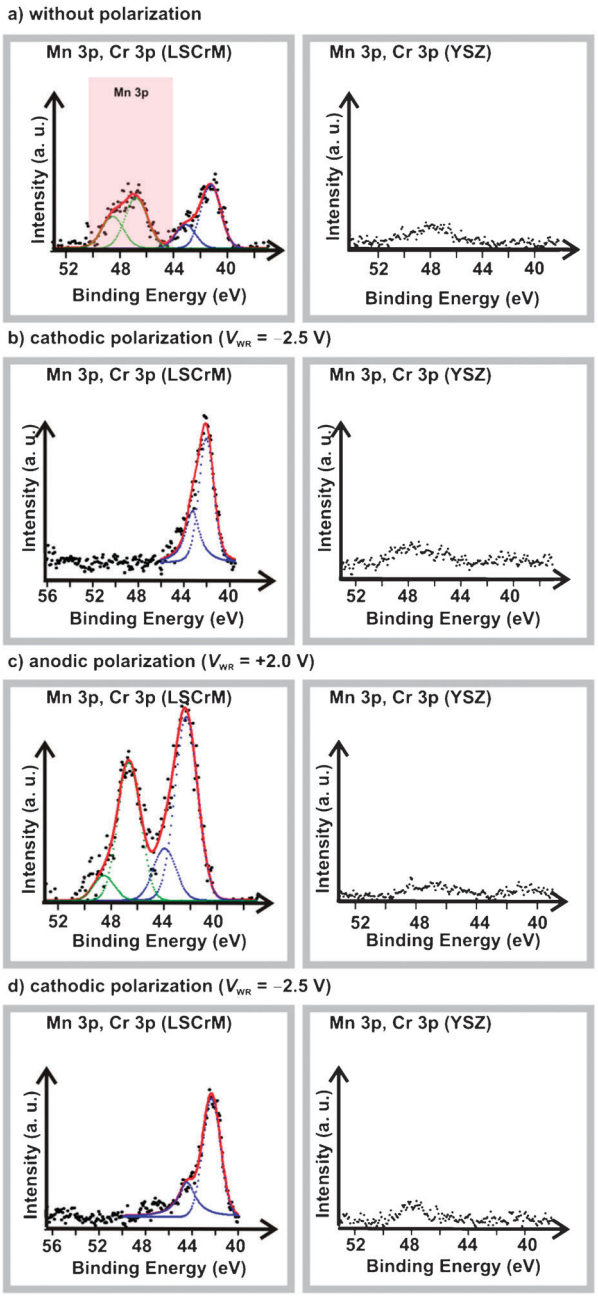

Fig. 7 *In situ* XPS measurements of the Mn 3p and Cr 3p peaks by different applied voltages monitored on the LSCrM (left) and the YSZ (right) surface with a distance of 50 μm away from the interface (tpb) at 600 °C.

are associated to ligand-to-metal charge transfer shake-up transitions.

Segregation of manganese under cathodic bias from the electrode surface onto the electrolyte has already been reported by Backhaus-Ricault *et al.*[6] in the case of LSM/YSZ electrodes. With *in situ* XPS and SPEM measurements the authors observed a pronounced diffusion of manganese out of the electrode onto the electrolyte by applying a cathodic potential. They concluded that the surface spreading of Mn^{2+} ions on the electrolyte is the reason for the improved electrochemical behavior under cathodic polarization because of direct oxygen incorporation into the electrolyte.

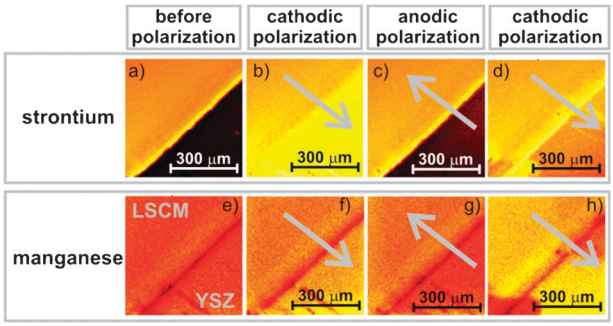

Fig. 8 *In situ* SIMS images of the interface (tpb) between LSCrM and YSZ at different applied bias. The measurements were performed at an oxygen partial pressure of 10^{-6} mbar and a temperature of 500 °C. All images were normalized by division of the corresponding total ion image. The brightness of the images was standardized so that in all secondary images of one element the same color corresponds to the same intensity.

For Cr a segregation onto the surface after cathodic polarization is visible. But the segregation of Cr remains constant during the other polarization steps. Therefore we can conclude that the influence of Cr segregation on the electrochemical performance is negligible.

It is important to note that corresponding to the observation of Sr and Mn, La shows an enhancement on the LSCrM surface under cathodic polarization and a depletion during anodic polarization. For Zr no concentration changes were observed during electrochemical polarization (see ESI†).

SIMS measurements

In the SIMS images bright colours represent high concentrations of the observed element and dark colours represent low concentrations. The SIMS imaging was performed at the interface (tpb) between the LSCrM and the YSZ surface.

The results for strontium show that under cathodic polarization a segregation of strontium onto the YSZ surface takes place (Fig. 8b and 8d) and a corresponding re-diffusion occurs under anodic bias (Fig. 8c). Thus, *in situ* SIMS measurements (Fig. 8) confirm the XPS results for Sr.

The Mn results demonstrate that the electrolyte surface is already covered with Mn before electrochemical polarization (Fig. 8e). This is probably a consequence of the high temperature treatment during sample preparation. Under cathodic bias the electrolyte surface becomes enriched in manganese (Fig. 8f). Applying an anodic potential causes the re-segregation of manganese onto the LSCrM surface (Fig. 8g). Indeed, as shown by SIMS as a strictly surface sensitive method, the low manganese concentration on YSZ found with XPS really results from a diffusion of manganese out of the LSCrM onto the electrolyte.

Additionally, SIMS depth profiles were measured to confirm the vertical diffusion of strontium between the surface and down to the bulk (see ESI†).

Discussion

Our *in situ* XPS and SIMS measurements show that the surfaces of LSCrM thin film electrodes on YSZ (111) are significantly enriched in strontium after annealing at 600 °C

for 10 hours. During cathodic polarization the LSCrM surface becomes depleted in strontium and manganese, and both elements diffuse into the bulk of the electrode and onto the electrolyte surface. The diffusion of the different species under cathodic bias is accompanied by an improvement of the electrocatalytic activity towards the oxygen reduction reaction as shown by impedance spectroscopy.

For LSM/YSZ electrodes an activation process for the O_2 reduction was reported in a number of studies[6,11–14,16] and at least four contrary explanations are discussed in the literature. The electrochemical activation under cathodic polarization has been attributed to (a) partial reduction of Mn(III+) to Mn(II+) with simultaneous generation of oxygen vacancies which leads to an enhanced oxygen ion transport,[12,20] (b) microstructural and morphological changes at the LSM/YSZ interface and at the surface and in consequence improved oxygen diffusion kinetics,[21–23] (c) removal or incorporation of passivating phases like SrO and MnO_x which inhibit surface oxygen exchange kinetics[11] or (d) extension of the active area for O_2 reduction by increased Mn(II+) concentration on the electrolyte surface and direct incorporation of oxygen into the electrolyte.[6]

In the case of LSM electrodes, Wang and Jiang[11] showed that the reduction of Mn(III+) and the formation of oxygen vacancies cannot explain the electrode activation. After current interruption a quick re-equilibrium state must be reached due to the fast anion diffusion. In fact the observed relaxation process is very slow and not in accordance with the proposed mechanism. Irvine *et al.*[24] found in oxygen isotopic exchange studies that the tracer oxygen diffusion coefficient for LSCrM is higher than the one reported for LSM. In consequence, the faster oxygen diffusion process in comparison to LSM electrodes must lead to an even faster relaxation behavior, but our measured relaxation times are in the same range as those of LSM electrodes. We conclude that this mechanism does not explain the observed activation of LSCrM electrodes.

We observed no morphological and structural changes after electrochemical polarization by XRD and HREM (see ESI†), and moreover, changes of the microstructure can rarely explain the large magnitude of the observed electrochemical activation.[25]

A mechanism proposed by Backhaus-Ricoult *et al.*[6] with direct incorporation of oxygen from the gas phase into the electrolyte due to a strong enrichment of Mn(II+) on the electrolyte surface and the increased electronic surface conductivity is possible. We found accumulations of manganese onto the YSZ surface but whether the oxygen reduction reaction can directly occur at this surface layer is hypothetical and has to be analyzed in further studies.

Evidence of strontium surface enrichment has been reported for other perovskite electrodes measured by XPS, AES and LEIS. Decorse *et al.*[26] first demonstrated a higher strontium surface concentration after sample preparation relative to the bulk composition of $La_{1-x}Sr_xMnO_{3\pm\delta}$ electrodes indicating SrO surface segregation. A small amount of SrO on the LSM surface after heat treatment under UHV conditions at 600 °C was also reported by Wu *et al.*[27]

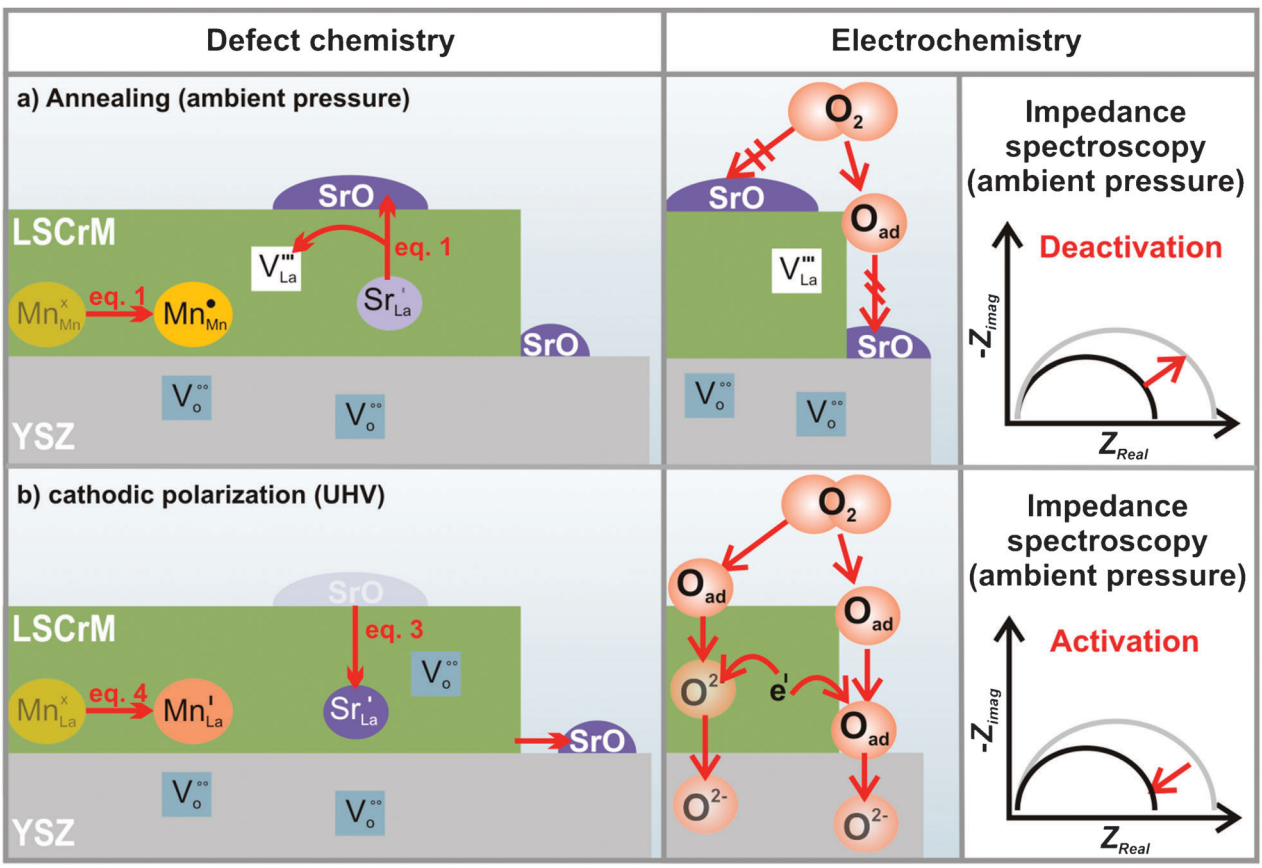

Fig. 9 Defect model for the explanation of the activation of LSCrM/YSZ electrodes by cathodic polarization.

Wang and Jiang[11] proposed a mechanism which involves incorporation of inhibiting SrO species into the LSM lattice under cathodic polarization and therefore a facilitated oxygen surface exchange reaction, resulting in the observed electrochemical activation. According to the existence of cation vacancies in the LSM defect structure the incorporation of SrO in the bulk should be a fast process which explains the pronounced activation especially in the first few minutes of cathodic polarization.

The presented results indicate that cation diffusion is also responsible for the observed activation under cathodic bias in this study and we propose a defect model (Fig. 9) based on the model of Wang and Jiang.[11]

The annealing process at ambient pressure causes the oxidation of manganese and segregation of strontium out of the LSCrM lattice with concomitant formation of cation vacancies (Fig. 9a). The strontium accumulation blocks the oxygen incorporation, and in consequence, deactivation of the cell is observed. The dominant defects in the material are cation vacancies.[28,29]

$$2Mn_{Mn}^{X} + Sr_{La}^{|} + \frac{1}{2}O_2 \rightarrow 2Mn_{Mn}^{\bullet} + V_{La}^{|||} + SrO_{(surf)} \quad (1)$$

By reducing the oxygen partial pressure (UHV conditions and high temperatures) the material appears to be in oxygen deficient region. The dominant ionic defects are oxygen vacancies. The charge neutrality is maintained by reduction of manganese ions by the following equation.[28]

$$2Mn_{Mn}^{X} + O_{O(LSCrM)}^{X} \rightarrow 2Mn_{Mn}^{|} + V_{O(LSCrM)}^{\bullet\bullet} + \frac{1}{2}O_2 \quad (2)$$

Under cathodic polarization (reduction) segregated surface-strontium is incorporated back into the LSCrM lattice with concomitant reduction of manganese ions (Fig. 9b). The removal of passivating SrO_{surf} enforces the surface exchange reaction. This is in agreement with our result that in the impedance spectra basically the low frequency intercept which characterizes the surface exchange reaction is influenced by electrochemical treatment.

$$V_{La}^{|||} + SrO_{(surf)} \rightarrow Sr_{La}^{|} + 2e^{|} + \tfrac{1}{2}O_2 \quad (3)$$

$$2Mn_{Mn}^{X} + 2e^{|} \rightarrow 2Mn_{Mn}^{|} \quad (4)$$

Anodic polarization increases the SrO concentration at the interface and electrode surface with decreasing electrochemical activation (backward reaction).

In contrast to our results Calliol *et al.*[17] found with XPS that cathodic polarization induces strontium segregation onto the LSM surface and La O′ *et al.*[16] suggested that under cathodic bias an excess of lanthanum near the three phase boundary is removed which inhibits oxygen reduction reaction. Up to now, our own experimental results cannot be explained with these mechanisms. Different reasons can be responsible for the observed differences. First of all our study was performed on LSCrM electrodes, the proposed activation mechanisms have all been suggested for LSM electrodes. Furthermore, cation segregation is controlled by temperature, oxygen pressure and polarization. Hence, the experimental findings are highly dependent on operational conditions and therefore different results may occur.

Conclusions

A strong performance improvement under cathodic polarization for the promising new electrode material LSCrM by impedance spectroscopy has been demonstrated. The electrochemical activation is strongly accompanied by surface segregation processes. For the first time, an electrochemically induced diffusion of different elements was analyzed *in situ* both by XPS and SIMS. The incorporation of strontium into the LSCrM surface according to the proposed mechanism by Wang and Jiang[11] seems to be the origin of the measured activation of the oxygen reduction reaction.

The understanding of performance improvement under electrochemical polarization is important for further applications of this alternative material in fuel cell technology. To get a deeper insight into the application possibilities of this new class of material experiments will have to be performed closer to the real working conditions of SOFCs. Therefore, *in situ* high pressure XPS measurements are currently planned. Moreover for the application in symmetrical SOFCs the electrode material must be stable under both oxidizing and reducing atmosphere. In consequence experiments under reducing conditions have to be performed. These studies complement and expand our previous XPS studies on simpler metal electrodes on YSZ.[30,31]

Acknowledgements

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